Oxygen Isotope Effect on ^{31}P NMR Spectra in the Phosphate Ion

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By Fourier transform high resolution NMR spectroscopy the ^{31}P signals of the phosphate species $^{31}P^{16}O_{4-n}{}^{18}O_n{}^{3-}$ ($n = 0, 1, 2, 3, 4$) have been resolved in aqueous solutions of potassium phosphate. An isotope effect on the Larmor frequency of $\delta(^{31}P) = (0.019 \pm 0.002)$ to lower frequency was found for the substitution of a ^{18}O atom for a ^{16}O atom in the phosphate ion.

It is well known, that in a molecule the substitution of a certain isotope for another influences the molecular properties. For many molecules changes in the Larmor frequencies have been observed if isotopes are substituted (see f. e. Ref. [1]). By increasing the resolution of the NMR spectra such isotope effects of the chemical shift can be measured even if the mass differences of the different isotopes are small such as for ^{16}O and ^{18}O or ^{32}S and ^{34}S (Ref. [2 − 11]). For some central nuclei in oxyanions oxygen induced isotope effects have been found [8, 9,].

Following the theory of Benedek et al. (Ref. [12]) Lauterbur [6] derived a simple relation, which describes the observed oxygen induced isotope effects in oxyanions fairly well [9, 10,]. In this theory the isotope effect of the chemical shift depends on the vibrational energies of the respective molecule. The theory predicts a lower Larmor frequency, if in the molecule with the heavier isotope the vibrational energies are smaller than in the molecule with the lighter one. This correlation is veryfied for example in the case of ^{55}Mn in MnO_4^- (Ref. [8, 9, 13]). For ^{95}Mo in MoO_4^{2-} − for these molecules to our knowledge no experimental values of the vibrational energies are known − also lower Larmor frequencies were observed [9, 10] for the species containing heavier isotopes.

For the PO_4^{3-} ion the vibrational energies are known to be higher in aqueous solutions for the $P^{18}O_4^{3-}$ than for the $P^{16}O_4^{3-}$ (Ref. [14]). This is

an anomalous behaviour [15] and has been explained by an isotope effect of hydrogen bonding in the solution, as in solid samples normal vibrational energies are measured [16]. It is interesting to know first, whether an isotope effect of the chemical shift of ^{31}P for the phosphate species $P^{16}O_4^{3-}$ and $P^{18}O_4^{3-}$ is observable at all and second, whether a lower Larmor frequency for the phosphate species containing heavier oxygen isotopes is found in spite of the anomalous vibrational energies or not. Measurements about this problem are reported in the following.

Experimental

The ^{31}P NMR signal was observed with a Bruker SXP 4 − 100 MHz spectrometer in a magnetic field of 2.11 T at 36.44 MHz. The magnetic field was internally stabilized by the ^{2}H lock B-SN 20. The free induction decays were accumulated and Fourier transformed by a B-NC 12 computer.

Solid P_2O_5 with the natural abundance of ^{18}O was dissolved in high-grade $H_2{}^{18}O$. The solution was concentrated by vacuum distillation until a syrup of phosphoric and diphosphoric acid remained which was rediluted by a bigger quantity of 99% $H_2{}^{18}O$. Sealed off in an ampoule the solution now was heated at 120 °C for 24 hours. Afterwards the phosphoric acid was neutralized by $K^{18}OH$ to the end point of phenolphthalein (pH 9.5) and the potassium orthophosphate concentrated toward crystalization in high vacuum. Since the oxygen exchange did not come to equilibrium during the heating the procedure resulted in an enrichment of 45 atom% ^{18}O of the product.

This solution was diluted with D_2O, which was used as lock-substance. The solution was made basic with NaOH to a pD value of about 14. 10 mm rotating cylindrical samples were used at (300 ± 3) K.

The chemical shifts are given as

$$\delta(X) = [(\nu_2 - \nu_1)/\nu_1] \cdot 10^6$$

following the convention of presentation of NMR data of heteronuclei [17].

Results and discussion

In Fig. 1 two spectra of different potassium phosphate solutions are given. For the signal A) an aqueous K_3PO_4-solution, which was enriched in ^{18}O to
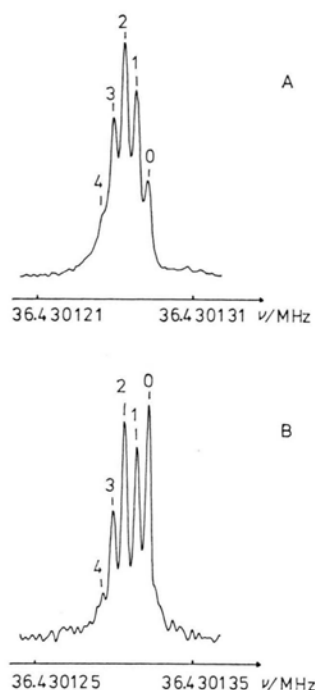
Fig. 1. ^{31}P NMR signals in aqueous solutions of potassium phosphate. The signals are from the right to the left due to the phosphate species $^{31}P^{18}O_n{}^{16}O_{4-n}^{3-}$ ($n = 0, 1, 2, 3, 4$). For signal A) a solution of K_3PO_4 enriched in ^{18}O to about 45% in D_2O was used. For signal B) K_3PO_4 enriched in ^{18}O and natural abundant Na_3PO_4 were dissolved in D_2O. The pD value of both solutions was about 14. The oxygen exchange is very slight for the phosphate ion and needs not to be taken into account [14]. For A) 19 FID and for B) 40 FID were accumulated. Further parameters for signals A) and B): experimental spectrum width: 200 Hz; pulse repetition frequency: 0.33 Hz; 1024 data points were accumulated followed by 7168 points of zero-filling for the Fourier transformation of 8 k points.

about 45% was used. One observes well resolved different signals with different intensities, which are from the right to the left due to the phosphate species $^{31}P^{16}O_{4-n}{}^{18}O_n^{3-}$ ($n = 0, 1, 2, 3, 4$). The enrichment has been determined from the intensities. To test the assignment a second sample was prepared by adding a natural abundant Na_3PO_4 solution, to the solution which was used for the spectrum A). The observed spectrum for this solution was the signal B) of Figure 1. One recognizes the increased intensity of the high frequency signal which therefore must be due to the $P^{16}O_4^{3-}$

species. Hence the amount of the oxygen induced isotope effect and the sign are known for ^{31}P in the phosphate ion: $\delta\,(^{31}P) = -(0.019 \pm 0.002)$ for substituting one ^{18}O nucleus for a ^{16}O nucleus. The negative sign means a shift to lower frequency. This small isotope effect of the chemical shift can only be observed for samples having very small ^{31}P NMR line-widths. The shift is further independent on the amount of the already substituted ^{16}O isotopes within the limits of error.

The amount of the isotope effect for ^{31}P is about one order of magnitude smaller than the amount observed for the transition metal nuclei ^{95}Mo or ^{55}Mn in the respective oxyanions [8 – 10]. This is in analogy to the larger chemical shifts measured for these nuclei: The substitution of a sulfur atom for an oxygen atom in PO_4^{3-} yields a chemical shift of the ^{31}P NMR signal of $\delta\,(^{31}P) = 33$ (Ref.[18]), whereas a chemical shift $\delta\,(^{95}Mo) = 500$ is found for the monothiomolybdate relative to the molybdate [19].

The ratio of these shifts is nearly the same as the ratio of the oxygen induced isotope effects. The sign of the oxygen induced isotope effect of ^{31}P in PO_4^{3-} can only be explained by the theory of Benedek et al.[12], if the vibrational energies of the excited states, which contribute to the shielding of the ^{31}P nucleus in PO_4^{3-}, compensate the anomalous difference in the vibrational energies of the ground state. As far as we know, no values of these vibrational energies in excited states have been determined until now. Pinchas and Sadeh [14] explained the anomalous vibrational energies in the ground state of PO_4^{3-} in aqueous solutions by isotope effects of the hydrogen bonding.

It seems, that the anomalous vibrational energies in the ground state of PO_4^{3-} do not determine the sign of the oxygen induced isotope effect of the chemical shift of ^{31}P. Even in this case one gets a shift to lower frequency if a heavier isotope is substituted as usually is observed [1 – 11].

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